

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL



REVISION NO. _____

Project No. E-19-619 GTRI/~~ORT~~ DATE 2/2/83Project Director: Dr. Allan S. Myerson School/~~Lab~~ Chemical Engr.Sponsor: National Science FoundationType Agreement: Grant No. CPE-8214246Award Period: From 2/1/83 To 7/31/85 (Performance) 10/31/85 (Reports)Sponsor Amount: Total Estimated: \$ 78,000 12-31-84 Funded: \$ _____Cost Sharing Amount: \$ 1,057 Cost Sharing No: E-19-312Title: Concentration Dependent Diffusion in Supersaturated SolutionsADMINISTRATIVE DATAOCA Contact Frank Huff x4820

1) Sponsor Technical Contact: Program Officer

Robert M. WellekProgram SectionDivision of Chemical and Process Engr.Directorate for NSFWashington, DC 20550 (202) 357-9606

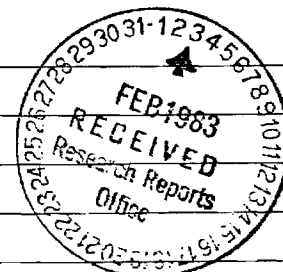
2) Sponsor Admin/Contractual Matters: Grants Official

Al RiceDivision of Grants & ContractsDirectorate for AdministrationNSFWashington, DD 20550(202) 357-9626Defense Priority Rating: N/AMilitary Security Classification: N/A

(or) Company/Industrial Proprietary: _____

RESTRICTIONSSee Attached NSF Supplemental Information Sheet for Additional Requirements.

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEETDate 8/14/86Project No. E-19-619School XXX Ch EIncludes Subproject No.(s) N/AProject Director(s) A. S. MyersonGTRC / XXXSponsor National Science FoundationTitle Concentration Dependent Diffusion in Supersaturated SolutionsEffective Completion Date: 12/31/84 (Performance) 3/31/85 (Reports)

Grant/Contract Closeout Actions Remaining:

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and no copies available for Library.
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E-19-619

Georgia Institute of Technology

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ATLANTA, GEORGIA 30332-0100

SCHOOL OF
CHEMICAL ENGINEERING
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May 16, 1984

Dr. R. Wellek
Thermodynamics and Mass Transfer Program
National Science Foundation
Washington, DC 20550

Dear Mr. Wellek:

Enclosed is the Annual Report on Grant # CPE 8214246,
"Concentration Dependent Diffusion in Supersaturated Solutions"
covering the first year of work on the project.

Sincerely,

Allan S. Myerson
Associate Professor

Enclosure

ANNUAL REPORT

NSF Grant # CPE8214246

CONCENTRATION DEPENDENT DIFFUSION IN
SUPERSATURATED SOLUTIONS

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Atlanta, GA 30332-0100

ABSTRACT

The diffusion coefficients of potassium chloride and sodium chloride were measured in concentrated, saturated and supersaturated solutions at 25°C employing Gouy interferometry. The results indicate a maximum in the diffusivity vs. concentration curve near saturation followed by a rapid decline in diffusivity toward zero with increasing concentration in the supersaturated region. This behavior supports the idea that the diffusion coefficient approaches zero at the spinodal concentration.

The data was successfully correlated by modifying an empirical activity coefficient equation (Robinson and Stokes (1955)) to account for molecular cluster effects and employing the calculated activity coefficients along with a predictive equation for diffusivity in electrolytes (Robinson and Stokes (1955)).

Scope

The study of diffusion coefficients in supersaturated solutions is of fundamental importance in further understanding the mechanism of diffusion and for the rational design of crystallization processes. Sorell and Myerson (1982) measured the diffusivity of urea in supersaturated aqueous solutions employing Gouy interferometry. Results of this study show a very rapid decline in the diffusion coefficient with increasing concentration in the supersaturated region. The rapid decrease in the diffusion coefficient with increasing concentration in the supersaturated region is similar to behavior observed in liquid-liquid systems near the consolute point. Claersson and Sundelof (1957) and Haase and Siry (1968) experimentally demonstrated that the diffusion coefficient rapidly declines toward zero as the consolute point is approached. Attempts have been made to explain this phenomena on thermodynamic grounds (Turner 1975, a,b)) and by postulating the failure of Fick's law near the consolute point (Anisimov and Perelman (1968)). Cussler (1980) explained this behavior by assuming that concentration fluctuations including both single molecules and clusters of molecules dominate behavior near the consolute point.

Gibbs derived a relation for the limits of stability of a fluid phase which consists of the locus of points defined by the relation:

$$\left. \frac{\partial \mu_1}{\partial X_1} \right|_{t,p} = 0 \quad (1)$$

On a phase diagram the locus of the points is known as the spinodal curve. The consolute point is a thermodynamic critical point

which means that $\partial\mu_1/\partial X_1 = \partial^2 U_1/\partial X_1^2 = 0$ hence the consolute point falls on the spinodal curve.

Equations for the prediction of diffusion coefficients in nonelectrolyte solutions are normally the product of an infinite dilution diffusivity and a thermodynamic correction term. The thermodynamic correction term in these equations are equivalent to $\partial\mu_1/\partial X_1$. The equations, therefore, predict that the diffusion coefficient should be zero at all points on the spinodal curve. Myerson and Senol (1984) predicted the location of the spinodal curve for the urea-water system and reported the results to be within 5% of the concentration obtained by extrapolating the data of Sorell and Myerson (1982) to a diffusivity of zero.

Equations for the prediction of diffusion coefficients in concentrated electrolytic solutions have had little success when compared to experimental data. Unlike nonelectrolytes in which the diffusion coefficient declines with increasing concentration over the entire concentration range, the diffusion coefficients of electrolytes first decline rapidly with increasing concentration and then usually rise becoming larger than the infinite dilution diffusivity at high concentrations. If the diffusion coefficients of electrolytes also approach zero at the spinodal curve there will be maximum in a plot of diffusion coefficient vs. concentration at the saturation concentration. It is the purpose of this paper to experimentally examine the diffusion coefficient of the electrolytes potassium chloride and sodium chloride in aqueous supersaturated solutions to further verify the hypothesis of a diffusivity of zero at the spinodal.

Conclusions and Significance

The diffusion coefficients of potassium chloride in water at 25°C were measured at concentrations ranging from 0.7M-4.23M. Experimental results in the undersaturated region were consistent to within 3% of those of Gosting (1950). Results show a maximum in the diffusivity vs. concentration curve near saturation (4.17M) followed by a rapid decline in the diffusivity with increasing concentration in the supersaturated region.

The diffusion coefficients of sodium chloride in water at 25°C were measured at concentrations ranging from 0.1M-5.46M. Experimental results in the supersaturated region were consistent to within 3% of those reported by Rand and Miller (1979). A maximum in diffusivity in the region of saturation followed by a rapid drop of diffusivity with increasing concentration was also observed.

It is postulated that this behavior is the result of molecular cluster formation and will result in a diffusivity of zero at the spinodal concentration. This behavior is consistent with observation in liquid-liquid (Haase and Siry (1968)) and non-electrolyte solid-liquid (Sorell and Myerson (1982)) systems near the spinodal curve.

An empirical relation for the predication of mean ionic activity coefficients was modified by making a parameter in the equation for the closest approach of ions a linear function of supersaturation. The activity coefficient data was then calculated and employed with a predictive diffusion equation (Robinson and

and Stokes (1958)) which has successfully correlated diffusivity data in the undersaturated region. Comparison of the calculation and experimental diffusion coefficients show agreement to within 1.5% for the potassium chloride system and to within 3% for the sodium chloride systems.

The results of this study indicate that the hypothesis of a zero diffusivity at the spinodal concentrations is confirmed by data in two electrolyte systems. Results also show that supersaturation diffusivity data can be correlated and/or predicted if the spinodal concentration is known.

Experimental Apparatus and Procedure

A schematic diagram of the Gouy interferometer apparatus employed in the diffusion studies appears in Figure 1. A detailed description of the apparatus can be found in Sorell (1981). Illumination of the system was provided by a Spectra Physics model 146 randomly polarized helium-neon laser. Fringe data were photographically recorded employing a lensless real image camera developed by O'Shea (1973). The diffusion cell employed in this study is a modification of cells described by Caldwell et al. (1957) and Sorell (1981) and appears in Figure 2. A single plexiglass temperature bath was used to control the temperature of the solution reservoir, valving, inlet and outlet tubing connected to the diffusion cell and the diffusion cell itself. In this way temperature gradients within the system and crystallization problems in the tubing were minimized.

The temperature in each bath was regulated by a Model 72 Immersion Circulator manufactured by Fisher Scientific. The control of temperature was 0.01°C .

The systems potassium chloride- H_2O and sodium chloride- H_2O were chosen for study because solubility (Seidell and Linke (1958)), density (Weast (1975)) and undersaturated diffusivity data (Rand and Miller (1979), Gosting (1950)) were available. In addition the viscosities of the supersaturated solutions were low enough to allow formation of a sharp boundary in the diffusion cell.

After solutions of the desired concentrations were prepared and the system brought to the appropriate temperature, the diffusion

cell was filled and the boundary sharpening procedure begun. A detailed description of this procedure can be found in Sorell (1980). The sharpness of the boundary could be qualitatively judged by the appearance of the fringe pattern observed during the process. When a fringe pattern of acceptable quality was obtained, flow to the diffusion cell from the solution reservoir was stopped. At this point the diffusion process is in the free diffusion mode. A timer was immediately started in order to record the difference in time between the beginning of free diffusion process and the subsequent photographic exposures of the Gouy fringe pattern.

The photographic exposures taken at each time were analyzed to yield experimental fringe distances between the undeviated slit image and each of the bottom eleven fringes in the photograph. This was done employing a comparator (model #267A) manufactured by the Gaertner Scientific Corp.

The total number of fringes present in the interference pattern (J_m) was determined from the fringe photographs employing a combination of the methods described by Tyrell (1961) and English (1947).

The analyses of the fringe photographs yielded an uncorrected diffusion coefficient for each photograph. A plot of these uncorrected diffusion coefficients vs $1/\text{time}$ extrapolated to $1/\text{time} = 0$ yields the true diffusion coefficient at the concentration $\bar{C} = (C_1 + C_2)/2$ (C_1 and C_2 are the concentrations of the solutions used).

Results and Discussion

Experimental values of the diffusion coefficient, D_{AB} , for the potassium chloride-water system at 25°C were obtained at different mean concentrations ($\bar{C} = (C_1 + C_2)/2$) ranging from 0.7M-4.23M. The concentration difference between the two solutions ($\Delta C = C_1 - C_2$) was 0.1M for all experiments. Experimental results at concentrations in the undersaturated region were compared to those reported by Gosting (1950) and were consistent to within 3%. The saturation concentration of potassium chloride in water at 25°C is 4.17M (Seidell and Linke (1958)). The results are shown in Figure 3 and show a dramatic decline in the value of the diffusivity with increasing concentration in the supersaturated region. Crystallization problems prevented measurements above a mean concentration of 4.23M.

Experimental results for the sodium chloride water system are shown in Figure 4. Measurements were made at mean concentrations ranging from 0.1M-5.46M with a concentration difference between the two solutions of 0.14M. Experimental results in the undersaturated region were compared to those of Rand and Miller (1979) and agreed to within 3%. The concentration of sodium chloride at saturation at 25°C is 5.32 (Seidell and Linke 1958). The results for the sodium chloride water system show the similar rapid decline in diffusivity with increasing concentration in the supersaturated region. The potassium-chloride-water system, however, has sharp maximum in the diffusivity vs. concentration curve at the saturation concentration while the sodium chloride-

water system exhibits a slight maximum at a concentration slightly less than saturation.

Extrapolation of the supersaturated diffusivity data to a diffusivity of zero yielded concentration values of 4.45M for potassium chloride and 5.6M for sodium chloride. These concentrations should be the spinodal concentration at 25°C.

Correlation of Experimental Data

In order to attempt correlation of experimental diffusivity data it is necessary to employ a thermodynamic correction term. In electrolyte solutions this requires that values of the mean ionic activity as a function of concentration be known. The Debye-Huckel equation can be used to calculate mean ionic activity coefficients at low concentrations.

$$\log \gamma_{\pm} = \frac{A |Z_1 Z_2| \sqrt{I}}{1 + B a \sqrt{I}} \quad (1)$$

The parameter a is defined as the distance from the center of an ion within which the center of no other can penetrate (Robinson and Stokes (1955)). In general the distance of closest approach is greater than the sum of the radii of the ions. This can be accounted for by hydration effects.

A two parameter model which has been shown to successfully fit (Robinson & Stokes (1955)) experimental activity coefficient data for a number of systems over a wide concentration range is given below:

$$\begin{aligned} \log \gamma_{\pm} = & - \frac{A |Z_1 Z_2| \sqrt{I}}{1 + B a \sqrt{I}} - \frac{n}{v} \log a_A \\ & - \log [1 + 0.001 W_A (v-n)m] \end{aligned} \quad (2)$$

Equation 2 fits experimental activity coefficient data in the sodium chloride water system from 0.1-5.0 molal with an average difference of 0.001 (Robinson and Stokes (1955)) and in the potassium-chloride-water system from 0.1-4.0 molal with an average difference

of 0.002 (Robinson and Stokes (1955)). The concept of the formation of molecular clusters in supersaturated solutions suggests that the average size of the parameter, \bar{a}° , the closest approach of ions would decline with the increasing number and size of the clusters. If the decline in \bar{a}° is assumed to be linear with supersaturation, Equation 2 can be rewritten as:

$$\log \gamma_{\pm} = - \frac{A |Z_1 Z_2| \sqrt{I}}{1 + B \bar{a}_O (1-JS) \sqrt{I}} - \frac{n}{v} \log a_A - \log [0.001 W_A (V-n)m] \quad (3)$$

where $\bar{a}^\circ = \bar{a}_O (1-JS)$

The maximum possible value of supersaturation that could be employed with Equation 3 would be the supersaturation at the spinodal curve. The parameter \bar{a}° will have its minimum value at that concentration, but still will be larger than the sum of the radii of the bare ions.

In order to make use of Equation 3 it is necessary to determine the constant J for each system of interest. This was accomplished by a trial and error procedure. A value of J was guessed and activity coefficients calculated over the entire concentration range to a concentration larger than the spinodal. The chemical potential was then calculated along with the derivative $\partial\mu_1/\partial X_1$ at the spinodal concentration. This procedure was repeated until a J was guessed which yielded a value of $\partial\mu_1/\partial X_1 = 0$ at the spinodal concentration. For potassium chloride J was found to be 2.0 ($n = 1.9$, $\bar{a}_O = 3.63 \times 10^{-10} \text{m}$ (Robinson and Stokes (1955) while $J = 4.3$ for sodium chloride ($n = 3.5$, $a_O = 3.97 \times 10^{-10} \text{m}$ (Robinson

and Stokes (1955)). The values of a at the spinodal curve calculated from Equation 4 are $3.25 \times 10^{-10} \text{m}$ and $3.07 \times 10^{-10} \text{m}$ respectively for potassium and sodium chloride compared with the sum of the radii of the bare ions of approximately $2.8 \times 10^{-10} \text{m}$.

A predictive equation that has successfully correlated diffusivity data of sodium and potassium chloride at high concentrations in the undersaturated region (Robinson and Stokes (1955) appears below:

$$D = (D^\circ + \Delta_1 + \Delta_2) \left(1 + m \frac{d \ln \gamma}{dm} \right) \left[1 + 0.036m \left(\frac{D_{\text{H}_2\text{O}}^{-n}}{D^\circ} \right) \right] \frac{n^\circ}{n} \frac{\eta^\circ}{\eta} \quad (5)$$

$$\text{where } \Delta_1 = - 8.03 \times 10^{-1} (t_2^\circ - t_1^\circ)^2 \sqrt{C} / (1 + 0.3286 \sqrt{C}) \quad (6)$$

$$\Delta_2 = 8.71 \phi_2 (0.3286 \sqrt{C}) \quad (7)$$

Employing equations 3-7 it was possible to calculate the diffusivity of potassium and sodium chloride over the entire undersaturated range and in the supersaturated range up to the spinodal concentration. A comparison of the calculated diffusion coefficients appear in Figure 5 and 6 for potassium chloride and sodium chloride respectively. The calculated values are within 1.5% of the experimental values for potassium chloride and within 3% for sodium chloride. The region of largest error in both systems is near the maximum in the diffusion vs. concentration curve.

The above results indicate that Equations 3-7 can be successfully employed to correlate experimental diffusivity data in the supersaturated region. This technique, however, could also be employed for the prediction of such data if the spinodal concentration can be obtained, or estimated. Myerson and Senol (1984) employed

an equation of state to estimate the spinodal concentration in the urea-water system. The spinodal concentrations of commonly crystallized materials can also be obtained from the crystallization literature by assuming the upper metastable limit (the concentration of maximum obtainable supersaturation) is approximately equal to the spinodal concentration.

It is postulated that the rapid drop in diffusion coefficients with concentration in the supersaturated region is the result of the formation of molecular clusters as a prelude to crystallization. The spinodal curve is known as limit of the "metastable zone," and the difference between the saturation and spinodal concentrations, the metastable zone width. If equilibrium is assumed to exist between all the various sized molecular clusters present in the solution, it is possible to calculate the number of each size cluster present by minimization of the Gibbs free energy (Ohara and Reid (1973)). Another approach to predicting the diffusion coefficient in supersaturated solutions is to calculate an overall diffusion coefficient based on a summation of the diffusion coefficients of all the clusters. A major problem with the approach is that the calculation of the size distribution of the clusters requires knowledge of the solid-liquid interfacial tension and is a very strong function of this parameter. The solid liquid interfacial tension is thought to be in the range of 1-100 ergs/cm² (Ohara and Reid (1973)). Employing this approach in the urea water system using a trial and error procedure, Chang (1984) found that an interfacial tension of 3 ergs/cm² resulted in diffusion coefficients within 10-40% of experimental data in

the supersaturated region. The failure of this technique to more accurately predict the concentration dependance of diffusivity in the supersaturated region could be the result of the interfacial tension varying with cluster size.

Acknowledgments

Financial support for this work was provided by the National Science Foundation through Grant CPE-8341721.

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5. Calculated vs. Measured Diffusion Coefficients of Potassium Chloride in Water at 25°C.
6. Calculated vs. Measured Diffusion Coefficients of Sodium Chloride in Water at 25°C.

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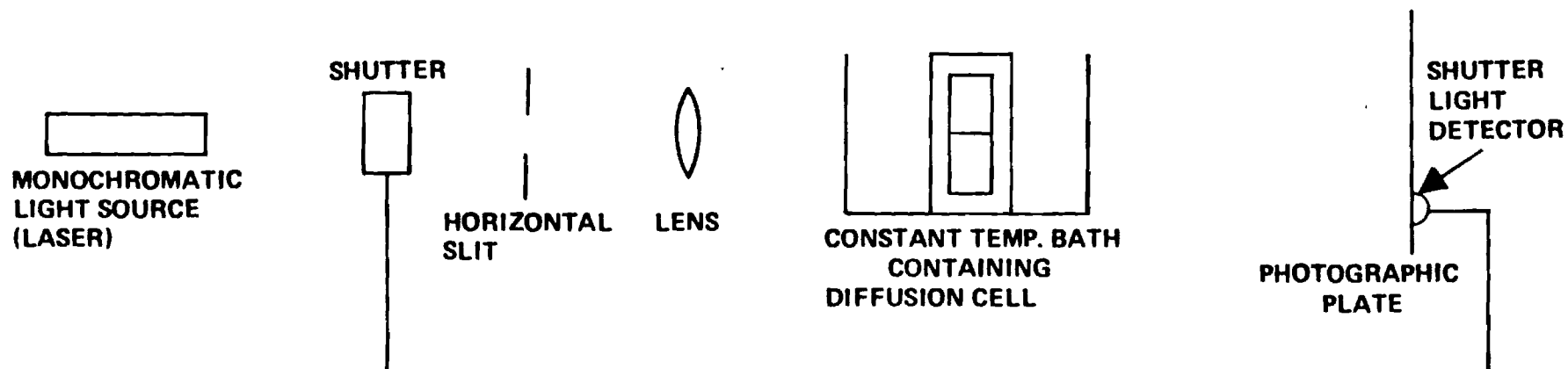
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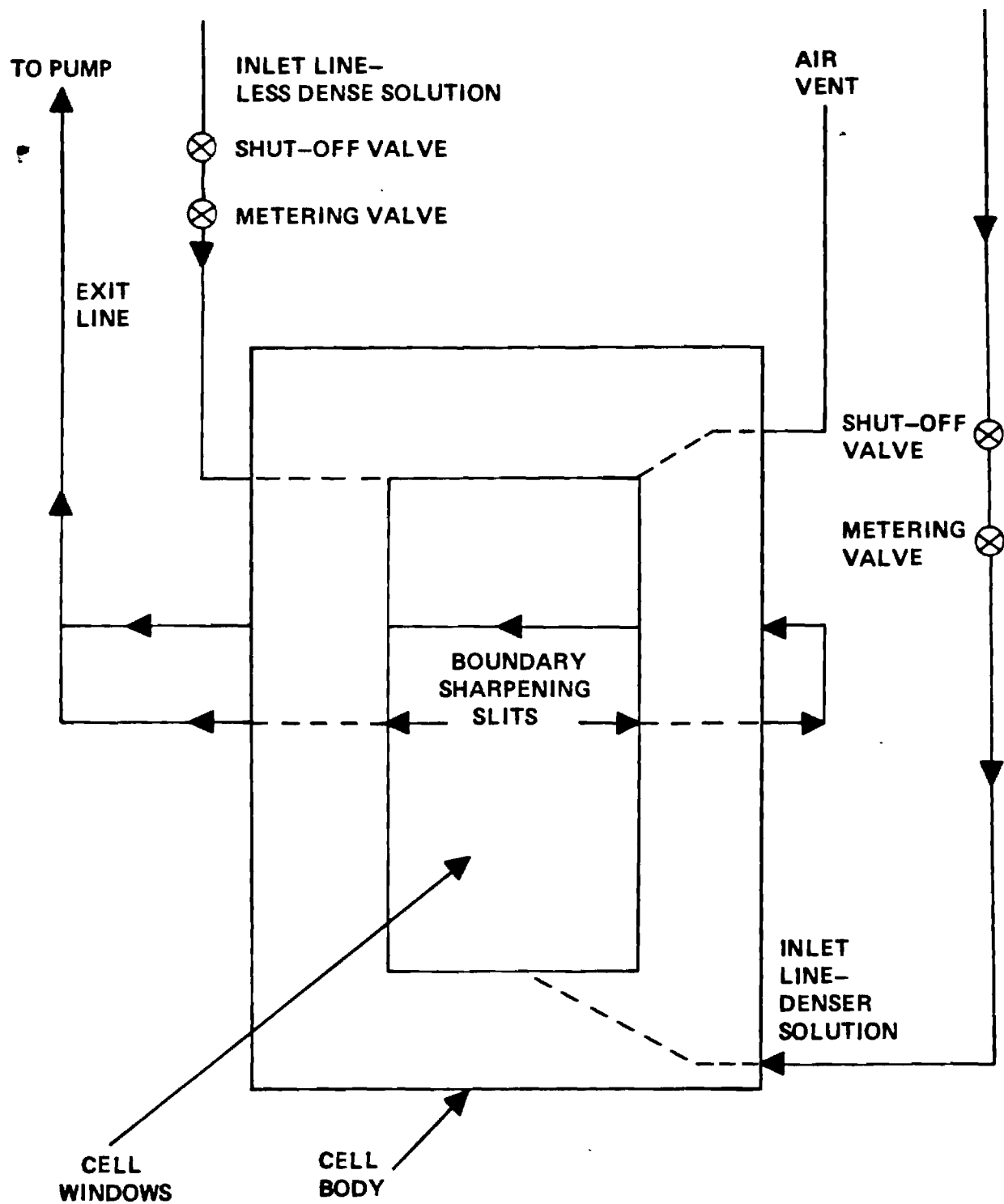
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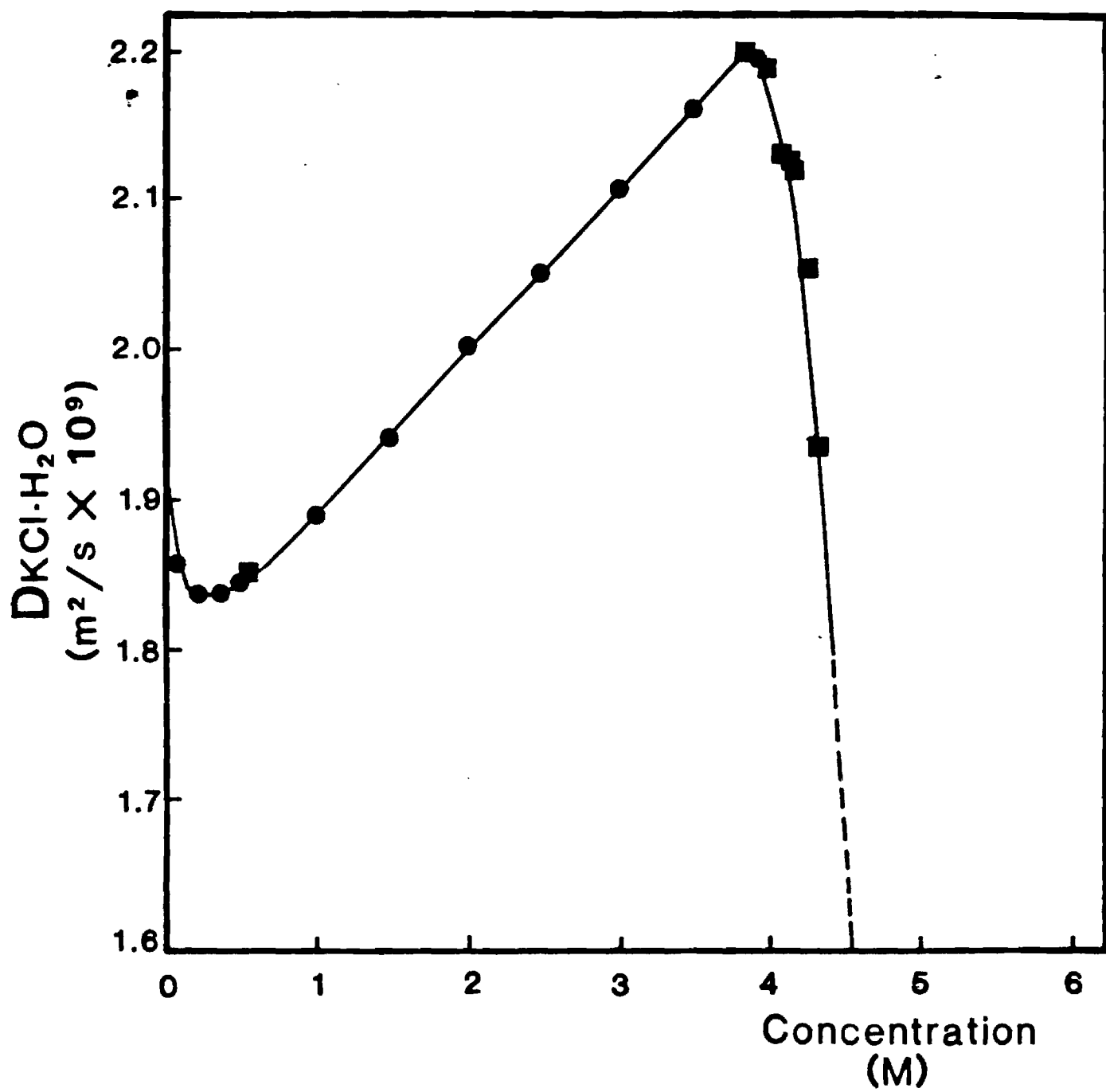
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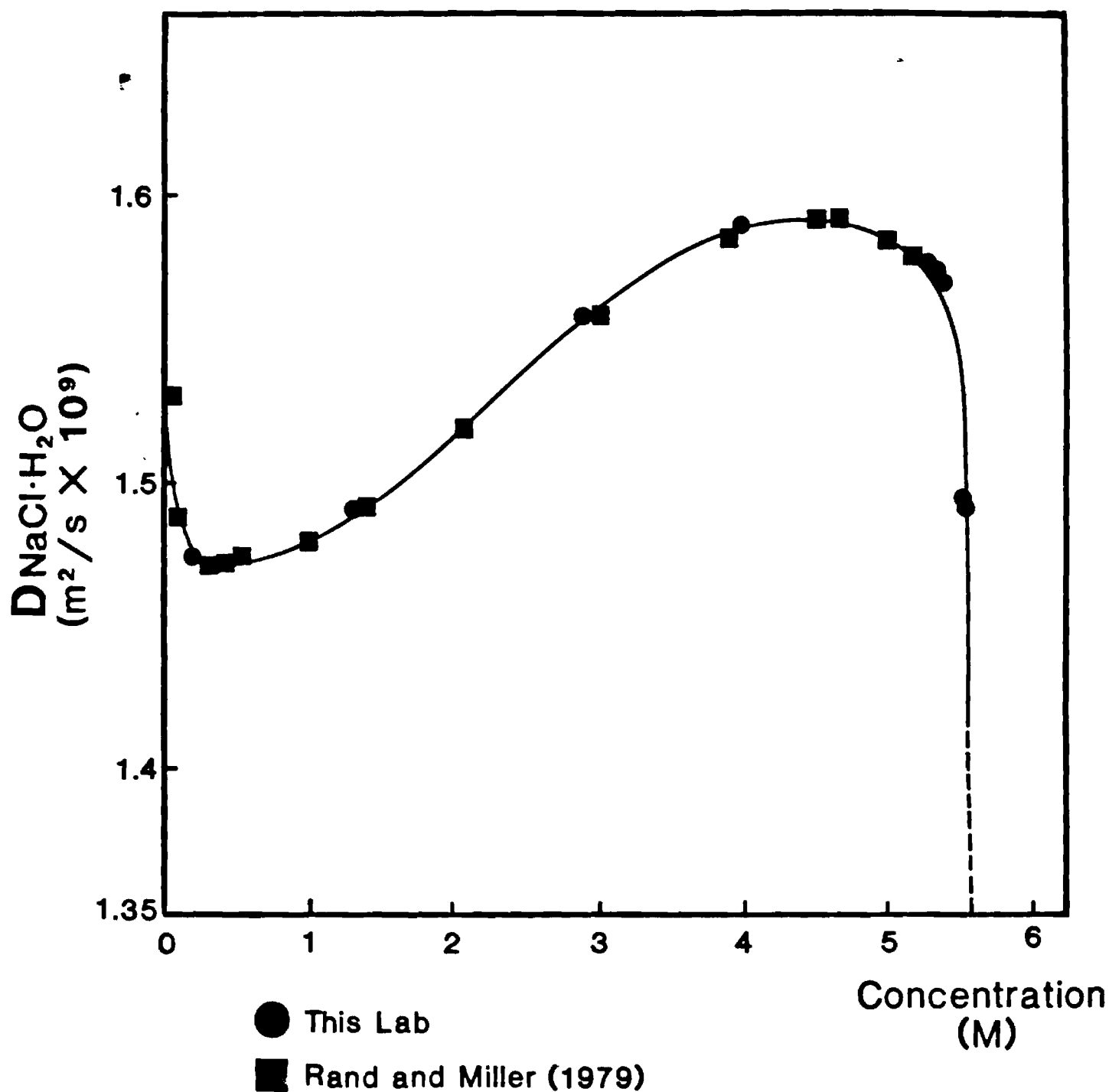


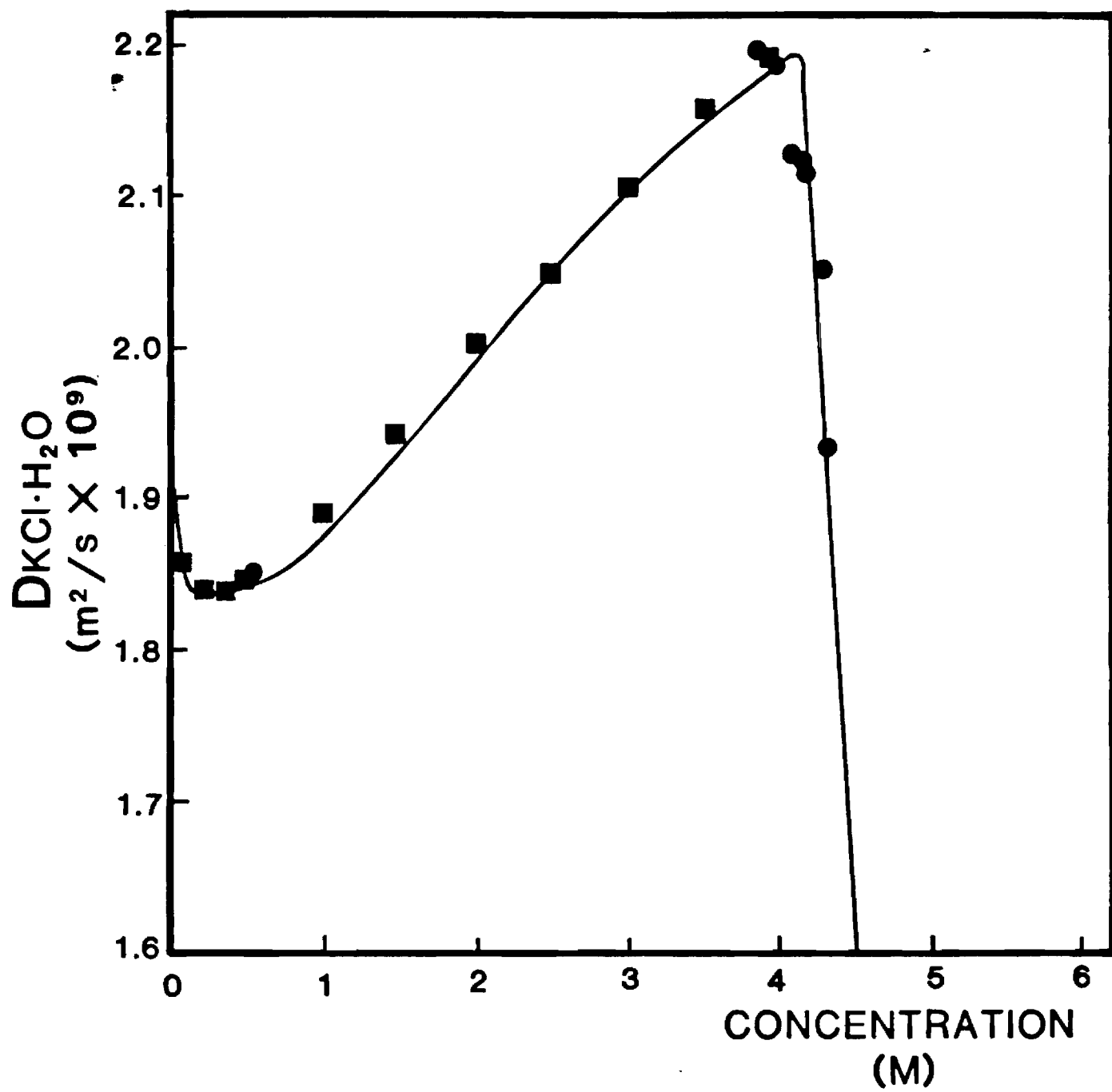




● Gosting (1950)

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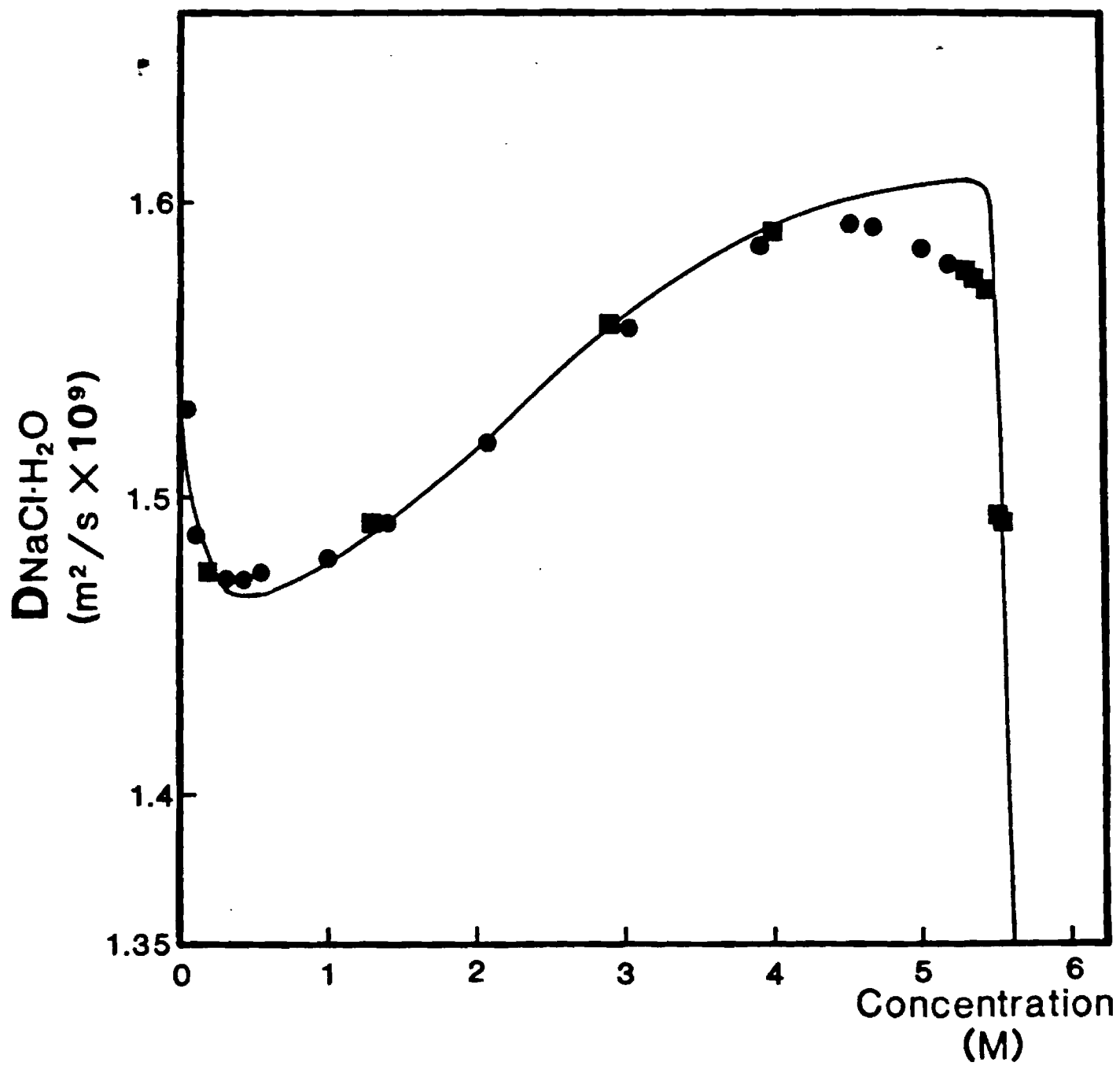




■ Gosting (1950)

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— Calculated



■ This Lab

● Rand and Miller

— Calculated

Nomenclature

A	constants Equations 1-3
B	coefficient of ion size from Equations 1-3
C	concentration (moles/liter)
D	diffusion coefficient
D^0	self diffusion coefficient
I	ionic strength
J	constant in equation
J_m	total number of fringes
M	molarity
S	supersaturation
W_A	molecular weight of A
\bar{a}	closest approach of ions
\bar{a}_0	closest approach of ions in undersaturated solutions
a_A	activity of substance A
m	Molality or meters
n	hydration number
A_1^0, A_2^0	ionic mobilities of anions and cations, respectively
x_i	mole fraction of species i
Z_1, Z_2	valences of cations and anions
Δ_n	n^{th} order electrophoretic correction to diffusion coefficient
γ_{\pm}	mean ionic activity coefficient
η_A	viscosity of species A
μ_i	chemical potential of species i
v	number of moles of ions formed from 1 mole of electrolyte
ϕ	molal osmotic coefficient